METHOD AND DEVICE FOR CONTROLLING AT LEAST ONE
OPERATING VARIABLE OF AN ELECTROLYTIC BATH

The present invention relates to a method for controlling at
least one operating variable of an electrolytic bath,
according to the preamble of Claim 1, and to a device for
implementing the method, according to the preamble of Claim 7.

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Galvanic methods are used for manufacturing workpieces having
coatings for corrosion prevention, for decorative purposes and
for preparations for paint work. An electroplating plant is
made up of a series of process baths, in each of which an

10   electrolytic plating process takes place, and of at least two
rinse baths per process bath, at least one rinse bath normally
being operated as a circulation rinse bath. The operating
variables of the processes proceeding in the baths must be
controlled and/or regulated as a function of different

15   parameters. If processes are controlled manually by an
operator according to the operator's store of experience, this
will result in strong fluctuations of the process conditions,
which leads to changing qualities of the electroplated
products and to a high consumption of process substances and

20   process adjuvants.

In the manual operation of an electroplating plant, the bath
compositions are monitored by concentration measurements in
samples, a manual withdrawal of the sample and an external

25   analysis of the sample being time-consuming and cost-intensive
and not allowing for a simultaneous control of the
electroplating operation. The composition of the process
baths directly affects the quality of the coatings. If the
concentrations of the active substances such as chromium,

30   nickel or zinc, for example, are too low in the process baths,
then the metals will be deposited incompletely and in

insufficiently thick layers. Furthermore, the process baths accumulate foreign ions through carryovers from previous baths and as a consequence of chemical reactions of the workpieces with foreign ions. This causes the layers to be deposited to become inhomogeneous and the inorganic corrosion protection or the preparation for the organic corrosion protection to be insufficient.

The rinse baths are used to rinse off the previously electroplated workpieces. This is to avoid carryovers with foreign ions into the subsequent process steps or into the environment. Rinse baths are recovered using ion exchangers or a reverse osmosis. Their preparation results in substantial quantities of waste water and sludges. The chemicals and waters withdrawn must again be fed into the electroplating plant as educts, which is uneconomical and ecologically dubious. This particularly applies when the rinse baths for reasons of producing a sufficient rinse effect are operated as circulatory rinse baths at a constant high volume flow. It is known to control the rinse bath composition according to the degree of contamination. Manually withdrawing samples from the rinse baths results in the disadvantages described with respect to the process baths.

DE 197 36 350 C1 describes a method for regulating the concentration of substances in electrolytes in which the content of oxidized redox ions in an electrolytic auxiliary cell is lowered to the precise extent to which metal is dissolved by the entered oxygen in the electrolyte. The regulation of the metal content occurs via the adjustable current of an auxiliary cell such that the overall electrolytic system is in equilibrium. Signals of an analyzer for determining the metal ion content of the metal to be deposited in the electroplating plant can be supplied to the current controller of the auxiliary cell.

The method for the electrolytic deposition of metals from electrolytes according to DE 44 05 741 C1 uses additives of organic process components to achieve certain physical

5   properties. To avoid complex concentration measurements, the organic additives are continuously added. An injection point in the pipeline system of an electrolyte circuit near an electrolytic cell may be chosen as the dosing point. The use of porous partition walls ensures that the organic process

10   compounds are located only in the cathode space which is free of the aggressive oxidized stage of the redox agent.

In the method for dosing process baths described in DE 196 00 857 A1, concentrates are added to the baths for

15   replenishing the ongoing consumption of chemicals. For this purpose, a portion of a used bath solution is continuously withdrawn, while at the same time fresh bath solution is added in the same quantity. A measurement of concentration is unnecessary.

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DE 197 27 939 A1 describes a method for dosing rinsing fluid in which the weight of a carried-over quantity of solution is determined by weight measurements of the object to be electroplated and if necessary of the support of the object.

25   From the measured carry-over values it is possible to calculate the resulting concentration changes in the respective bath stations. This is done by a data processing system to which an open-loop or closed-loop control circuit for the dosing of rinsing water is connected such that

30   slightly changed solution concentrations can be automatically adjusted to a setpoint value.

Furthermore, it is known from WO 00/00811 A2 to use the methods of laser Raman spectroscopy for analyzing

35   pharmaceutical substances.

JP 11118796 A shows a system for analyzing proteins in urine, in which a urine sample is mixed with a diluent and a dyeing agent and is supplied via pipelines to an optical scattered

5   light analyzer. In the scattered light analyzer, the sample fluid is exposed to laser light. The composition of the scattered light changes as a function of the protein content of the sample fluid. The analysis time and the quantity of the sample fluid are changed as a function of the absorption

10 of the measured light.

In the system for optical substance analysis shown in EP1 059 708 A1, a substance sample is exposed to a bundled laser light. The substance interacts with the laser light.

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The cited methods of substance analysis are concerned with the investigation of individual samples which are prepared at the site of the analysis system and are supplied to the analysis system. With respect to the handling of the samples and with

20 respect to the interaction with open-loop and closed-loop control devices, the analysis systems are not designed for the process control of electroplating plants.

The objective of the present invention is to develop a method

25 and a device for controlling at least one operating variable of an electrolytic bath, which allow for the production of coatings of improved quality, while reducing the use of chemicals.

30 This objective is achieved by a method having the features as recited in Claim 1. A device having the features recited in Claim 8 is suitable for implementing the method. Advantageous refinements derive from the dependent claims.

The method for controlling at least one operating variable of an electrolytic bath is based on the measurement of concentration of a bath component using an electromagnetic radiation which excites the sample taken from the bath in such

5   a way that light is emitted. The concentration may be ascertained from the spectrum of the emitted light. Using the measured concentration values it is possible to control or regulate various operating variables. In this context, an operating variable is understood in the broadest sense as any

10   physical variable, the change of which influences the quality of a coating and the quantity of the chemicals used. Important operating variables are, for example, the composition of the bath, the bath temperature, the movement of the electrolyte and of the objects to be galvanized, the

15   degree of contamination or the electric current in a bath.

The present invention is used to control or regulate an electroplating plant with the aid of a process-integrated analysis, the analysis being preferably based on the laser-

20   induced emission spectral analysis. Using the laser-induced emission spectral analysis, it is possible to control the contamination of a galvanic bath or rinse bath in an advantageous manner. A system for the laser-induced emission spectral analysis preferably contains a laser, which is used

25   to vaporize, by a number of laser pulses, a fluid sample withdrawn from the bath. The quantity of the fluid is small, e.g. having a volume of less than 1 ml.

The ionogenic composition of the substances contained in the

30   fluid is determined by a downstream spectrometer. It is essential that the contactless measuring method has no or only a slight sensitivity to contamination by foreign ions. The measuring process allows for a rapid bath analysis without complicated sample preparation. A measuring time of less than

35   three second can be achieved in practice, which represents a

quasi simultaneous detection of the state of a bath. A
decomposition of the sample is not required. The time-
resolved measurements of the concentrations may be made
without the use of a protective gas at air atmosphere. The
spectroscopic measured values are transmitted to a computer
which is part of the open-loop or closed-loop control system
of the electroplating plant. As the result of the execution
of a measured value processing program, control outputs for
control elements are generated which control e.g. the re-
sharpening or discharging of a process bath when specified
concentrations of process bath or interfering substances are
undershoot or exceeded. This also provides for the
possibility of controlling the regeneration of the process
bath, e.g. using diffusion analysis in acidic scouring or
diaphragm electrolysis in chromium-containing process
solutions, via concentration measurements of interfering
components. In addition to optimizing the electroplating
operation, this is used especially for a process-integrated
quality assurance since the process bath quality directly
influences the result of electroplating.

If the ionogenic contaminations in the rinse baths are
measured, then this allows for a control of the rinse bath
regeneration, i.e. of the volume flow to be regenerated. This
allows for the use of energy, process adjuvants such as
coagulants and precipitants, and of water or waste water to be
minimized.

In order to prevent the intermixing of the individual process
baths and thus a falsification of the measured values, samples
from each bath are separately supplied to the spectrometer via
a decentralized pipeline system. With regard to a good
mixture it is advantageous if high flow velocities of the
sample fluids are achieved in the pipes of the pipeline
system. At low sample volumes, the pipeline system may be

provided in a cost-effective manner having small flow cross-
sections. The separate pipeline system saves time-consuming
and costly in-between cleanings of the pipelines using
distilled water and subsequent drying using compressed air,

5   which would be necessary if all baths were connected to the
spectrometer via only one sample feed.

In a variant of the device for controlling at least one
operating variable of an electrolytic bath, the pipeline

10   system ends at a sample plate, it being possible for the
sample fluid from a particular bath to be squirted
automatically and in a clocked manner onto the sample plate.
A sample plate may take the form of a carousel for individual
samples, laser light acting directly onto a sample on the

15   sample plate. Following the analysis of the light emanating
from the sample, the sample is removed from the sample plate
using suitable cleaning devices and the sample plate is
provided with a fresh sample. The sample plate may be
provided with samples of only one bath as well as samples from

20   different baths.

The spectroscopic measured values obtained may be transmitted
directly to a master computer of the electroplating plant for
calculating control outputs. For a process-integrated quality

25   assurance, the measured data may be stored for archiving the
bath states, particularly the process bath states. There is
the possibility of recording the time-dependency of the
concentrations and the detection of concentration intervals.
The method and the device allow for the process-integrated

30   detection particularly of aluminum, copper, cadmium, chromium,
iron and zinc as well as of other elements in process and/or
rinse baths. It is possible to ascertain concentrations of
the mentioned substances in the process baths in the range of
1-100g/l and in the rinse baths in the range below 100ppm.

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The present invention will be explained below with reference
to an exemplary embodiment. Figure 1 shows a schema of an
electroplating plant for implementing the method.

5   The electroplating plant is made up of two containers 1, 2 for
process baths 3, 4 and of four containers 5-8 for rinse baths
9-12, which in the process sequence are respectively
downstream of process baths 3, 4. Salt of a coating metal is
dissolved in each of process baths 3, 4. Workpieces 13 to be
10 coated are suspended from carrier devices 14, which are
connected to conveyer devices. Workpieces 13 are completely
immersed in a process bath 3, 4 or rinse bath 9-12. Via
carrier device 14, workpieces 13 in process bath 3, 4 are in
each case connected to the negative pole 15, 16 of a
15 controllable power source 17, 18. Process baths 3, 4 moreover
contain electrodes 19, 20 leading to the positive pole 21, 22
of the respective power source 17, 18. When current flows
through process baths 3, 4, atoms of the coating metal are
deposited by a chemical reduction onto previously thoroughly
20 cleaned workpieces 13. To maintain the equilibrium between
the atoms deposited on workpieces 13 and the atoms contained
in salt solutions of the coating metal, a dosing device for
the salt is located on each process bath 3, 4. A dosing
device is made up of a reservoir 23, 24 for a highly
25 concentrated saline solution 25, 26, an intake line 27, 28, a
dosing pump 29, 30, a connecting line 31, 32, a controllable
dosing valve 33, 34 and an outlet 35, 36. For regenerating
rinse baths 9-12, dosing devices are likewise provided, which
for each rinse bath 9-12 are made up of a reservoir 37-40 for
30 a non-contaminated rinse bath fluid 41, 44, an intake line 45-
48, a dosing pump 49-52, a connecting line 53-56, a dosing
valve 57-60 and an outlet 61-64.

For monitoring the concentration of the coating metals in
35 process baths 3, 4 and the degree of contamination by foreign

ions in process baths 3, 4 and in rinse baths 9-12, a device
65 for laser-induced spectral analysis is provided. Device 65
includes a sample plate 66 having concentrically arranged
sample hollows 67. Sample plate 66 is situated in such a way

5   that it is able to rotate about its center axis 68 with the
aid of a stepping motor 69. Device 65 is connected via a
pipeline system to process baths 3, 4 and rinse baths 9-12.
For each process bath 3, 4 or rinse bath 9-12, the pipeline
system comprises an intake line 70-75, a pump 76-81, a

10   connecting line 82-87, a controllable valve 88-93 and outlet
lines 94-99, which in each case lead to a sample hollow 67.
Device 65 furthermore comprises a laser 100, the beam 101 of
which points to the reference circle 102 of sample hollows 67
on sample plate 66. Device 65 furthermore includes a

15   spectroscope 103 having an imaging system 104 and a radiation
receptor 105. A cleaning device for sample hollows 67 is
associated with device 65. The cleaning device is made up of
suction line 106 beginning at reference circle 102, a suction
pump 107 and a line 108 leading to a waste container 109.

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For controlling and regulating the composition of process
baths 3, 4 and rinse baths 9-12, an open-loop and closed-loop
control device 110 is provided which can be part of a control
station of the electroplating plant. In addition to display

25   and operating devices, power supply devices, signal converter
and processing systems and control elements, open-loop and
closed-loop control device 110 comprises a computer 111.
Computer 111 is made up of a central processor 112, which is
connected via a bus system 113 to a hard disk drive 114, a

30   random access memory 115 and a read-only memory 116. A
keyboard 117 and a screen 118 are connected to bus system 113.
Central processor 112 is used for the temporal coordination
and control of all elements connected to bus system 113.
Random access memory 115 is used for storing temporary

35   instructions or data. Read-only memory 116 contains

invariable instructions, data and programs, which are required
for the correct functioning of computer 111. Hard disk drive
114 is a memory having a large capacity for storing programs
and data for the implementation of the processing of measured

5   values and the calculation of control variables. Keyboard 117
allows for the input of data on the part of an operator.
Screen 118 is used to issue data and instructions to the
operator. Via measurement and control lines 119 represented
as dashed lines and using suitable interfaces, dosing valves

10   33, 34, 57-60, valves 88-93, power sources 17, 18, suction
pump 107, stepping motor 69, laser 100 and spectroscope 103
are connected to bus system 113.

     Using the electroplating plant described above, the method can
15   be implemented as follows:

     With the aid of carrier devices 14 and the said conveyer
devices, workpieces 13 are transported in succession through
process bath 3, rinse baths 9, 11, process bath 4 and rinse

20   baths 10, 12. In the passage through process baths 3, 4, the
galvanic salt solutions deplete of ions of the coating metal.
In the passage through rinse baths 9-12, the rinse solutions
are contaminated with foreign ions. The method according to
the present invention is based on continuously measuring the

25   concentrations of the coating metal ions in process baths 3, 4
and the degrees of contamination of process baths 3, 4 and of
rinse baths 9-12 with foreign ions using device 65. For this
purpose, small quantities of process baths 3, 4 and rinse
baths 9-12 are in each case transported by pumps 76-81 through

30   connecting lines 82-87, valves 88-93 and outlet lines 94-99
into one of sample hollows 67. For this purpose, open-loop
and closed-loop control device 110 briefly opens one of valves
88-93 such that, in accordance with the program specified by
computer 111, samples of one or several process baths 3, 4 or

35   rinse baths 9-12 are provided on sample plate 66 for measuring

using device 65. Stepping motor 69 causes sample plate 66 to rotate about center axis 68 such that a sample hollow 67 together with a sample is brought into the direction of beam 101 or the optical axis of the path of the measuring beam of

5   spectroscope 103. Laser beam 101 excites the sample in a short time in such a way that the sample emits light, which for spectral analysis strikes through optical system 104 onto radiation receptor 105. The spectrum of the light on radiation receptor 105 is characteristic for the elements

10   contained in a sample and their concentrations. The measured values of spectroscope 103 are supplied to computer 111 where they are processed.

If the concentrations of the coating metal ions in process

15   baths 3, 4 fall below specified threshold values, then control commands are output to dosing valves 33, 34 via bus system 113 such that dosing valves 33, 34 open for specified time spans. While a dosing valve 33, 34 opens, concentrated saline solution 25, 26 is supplied by dosing pumps 29, 30 to the

20   respective process bath 3, 4 for refreshment. Concentrated saline solution 25, 26 intermixes with the depleted process bath solution such that the concentration of the coating metal ions is essentially kept constant aside from small deviations.

25   The time characteristic of the growth of a coating on workpieces 13 may be influenced by adjusting the current flow in the process baths. For this purpose, control signals are sent from open-loop and closed-loop control device 110 to power sources 17, 18.

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If the concentration of the foreign ions in rinse baths 9-12 exceed specified threshold values, then opening instructions are sent from open-loop and closed-loop control device 110 to dosing valves 57-60. As dosing valves 57-60 are opened for a

35   specified duration, fresh rinse bath solution is supplied to

the respective rinse bath 9-12, while used rinse bath solution
is removed.

Following the analysis of a sample in a sample hollow 67,
5   sample plate 66 is rotated further by stepping motor 69 such
that the respective sample hollow 67 reaches the location of
suction line 106. Via bus system 113, suction pump 107
receives an activation signal which puts suction pump 107 into
operation and thus removes the rest of the sample from sample
10   hollow 67 into waste container 109.

The device according to the present invention is not limited
to the exemplary embodiment shown. The equipment of the
pipeline system with pumps 76-81 and valves 88-93 is only
15   exemplary. Instead of sample plate 66, device 65 may be
equipped with other devices for handling samples. In place of
suction pump 107 and suction line 106, other suitable cleaning
devices for sample containers may be provided. Likewise the
means for refreshing process baths 3, 4 and for regenerating
20   rinse baths 9-12 may be designed differently than described.
Furthermore, the number of process baths 3, 4 and rinse baths
9-12 may be adapted to the prevailing requirements.

List of Reference Symbols Used

1, 2	container	68	center axis
3, 4	process bath	69	stepping motor
5-8	container	70-75	intake line
9-12	rinse bath	76-81	pump
13	workpiece	82-87	connecting line
14	carrier device	88-93	valve
15, 16	negative pole	94-99	outlet line
17, 18	power source	100	laser
19, 20	electrode	101	beam
21, 22	positive pole	102	divided circle
23, 24	reservoir	103	spectroscope
25, 26	saline solution	104	imaging system
27, 28	intake line	105	radiation receptor
29, 30	dosing pump	106	suction line
31, 32	connecting line	107	suction pump
33, 34	dosing valve	108	line
35, 36	outlet	109	waste container
37-40	reservoir	110	open-loop and closed-loop-control device
41-44	rinse bath fluid	111	computer
45-48	intake line	112	central processor
49-52	dosing pump	113	bus system
53-56	connecting line	114	hard disk drive
57-60	dosing valve	115	access memory
61-64	outlet	116	read-only memory
65	device	117	keyboard
66	sample plate	118	screen
67	sample hollow		